SPONTANEOUS GENERATION OF HEAT IN RECENTLY HARDENED STEEL. III.

By CHARLES F. BRUSH.

(*Read April 13, 1917.*)

The present paper is the third of a series under this title. In the first paper[1] it was shown that a specimen of carbon tool steel, and also a specimen of "high-speed" tungsten-chromium steel after hardening by water quenching at a high temperature, spontaneously generated heat in appreciable quantity for at least several weeks, the rate of generation steadily diminishing. It was also shown that the carbon steel, after hardening, shrank progressively when tempered to "straw" color, to "light blue" and finally annealed. It was further shown that another specimen of high-carbon steel, after hardening, spontaneously shrank in measurable amount for many days, the rate of shrinking steadily diminishing. The plotted curve of spontaneous shrinkage was strikingly similar to a curve (not plotted) of total heat spontaneously generated in the other specimen of carbon steel, showing an apparent relationship between the two phenomena. But it was pointed out that spontaneous shrinking could not possibly be the prime cause of the spontaneous generation of heat observed because it was wholly inadequate in amount. This conclusion was afterward confirmed (second paper) in the cases of two specimens of nickel-chromium steel which, after quenching just above the temperature of decalescence, spontaneously generated heat freely but did not shrink at all.

The second paper,[2] after reviewing the first, treated principally of two specimens of nickel-chromium steel furnished for this investigation by Sir Robert Hadfield. Each specimen consisted of twelve

[1] *Proc. Am. Phil. Soc.*, Vol. LIV., No. 217, May–July, 1915.

[2] *Physical Review*, N. S., Vol. IX., No. 3, March, 1917. *Proc. Royal Soc.*, Series A, Vol. 93, No. A649, April 2, 1917. Joint paper with Sir R. A. Hadfield.

half-inch round bars five inches long, like in size and number those of each of the steels of the first paper, so that results obtained were quantitatively comparable with the earlier ones. Each specimen was first hardened by quenching at a temperature just above that of decalescence as indicated by almost complete loss of magnetic susceptibility.

For observing the magnetic behavior of the steel while being heated or cooled in the gas furnace employed, the bundle of bars was surrounded by a single turn of asbestos-insulated platinum wire, the ends of which were connected with a ballistic galvanometer having the usual mirror and scale. The furnace was surrounded by a large coil of heavy copper wire through which a direct electric current could be established and broken at will by means of a switch and storage battery. Before the steel bars were placed within the platinum loop inside the furnace, closure of the outer copper coil circuit caused a brief electric pulse in the loop and a "kick" in the galvanometer, giving a definite minimum deflection easily observed with considerable precision. With the steel bars inside the platinum loop the galvanometer deflection was, of course, many times greater until, with rising temperature, the decalescent point was approached; then the deflection fell rapidly to the minimum value as above, or very near it. This simple induction apparatus was found entirely reliable and satisfactory.

Each of the nickel-chromium steels exhibited good generation of heat after hardening as above.

They were again heated, to a temperature considerably above decalescence, and quenched as before. This second hardening induced a greater generation of heat than the first hardening, especially in the case of specimen B.

Specimen B was slowly heated a third time, somewhat above the temperature of complete loss of magnetic susceptibility, and allowed to cool very slowly in the furnace until complete recovery of magnetic susceptibility was attained; then it was immediately quenched. A very fair generation of heat followed this treatment. This was quite unexpected because it was thought that true hardening of the steel could not have taken place. In the absence of suitable apparatus no test of hardness was at that time made. The twelve bars (specimen B) were next annealed by slowly heating to full decalescence and then allowing to cool very slowly in the furnace. As expected, no trace of heat generation followed this treatment which was made for checking purposes.

Before commencing the experiments with specimens A and B, a test bar of each lot was prepared for accurate length measurements which followed each treatment. The very interesting results of these measurements, differing materially in the two specimens, were tabulated and compared.

The present (third) paper deals with some later experiments prompted by the anomalous behavior of specimen B of the Hadfield nickel-chromium steel after its third quenching described above.

In conducting these experiments an electric furnace was employed for heating, instead of the less convenient gas furnace formerly used, and the latest form of "sclerescope" for testing hardness was installed; also, a most modern industrial thermo-electric pyrometer. The latter was used as it came from the maker, without further calibration; hence the temperatures recorded in this paper may be several degrees in error, though they are thought to be relatively consistent.

The apparatus employed in detecting, measuring and following the progress of heat generation in the steels under treatment was fully described and illustrated in each of the former papers, and it is thought best to omit another description here.

It will be recalled that "specimen B" was left in the annealed condition. In this condition it was subsequently found to have a scleroscope hardness of 31. This is the mean of many consistent measurements. Each scleroscope hardness cited in this paper is the mean of at least ten consistent measurements, each measurement made on a fresh spot of surface carefully made smooth and flat.

In order to ascertain the critical temperatures of decalescence and recalescence of "specimen B," three of the twelve bars were very gradually heated until almost complete loss of magnetic susceptibility was reached. This occurred rather abruptly at about

777° C. One of the bars was quenched at this temperature, and its scleroscope hardness was found to be 74. This may be taken as the hardness of "specimen B" after the first quenching described in connection with the second paper.

The remaining two bars were allowed to cool very slowly in the furnace until complete recovery of magnetic susceptibility took place at about 660°. Recovery was abrupt in temperature. One of these bars was quenched at this temperature, and its hardness was found to be only 37, which is not much above annealed hardness (31). This seems to me conclusive evidence that true hardening did not take place in "specimen B" on its third quenching already described

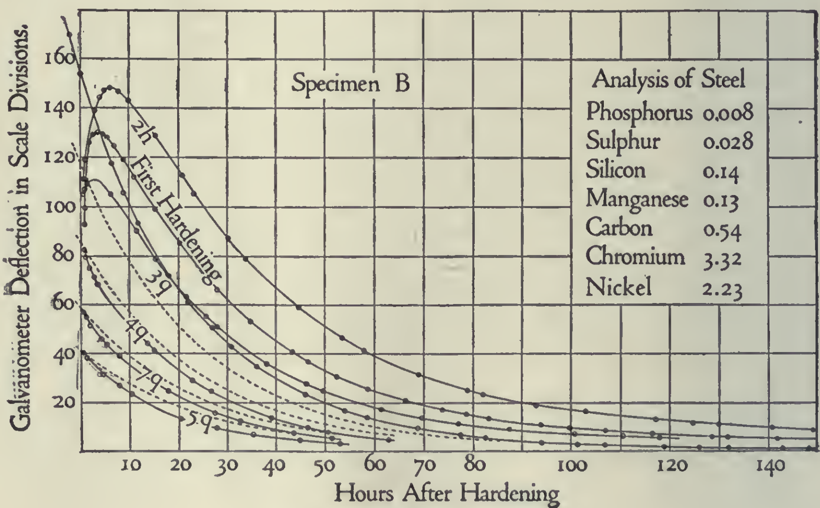

FIG. 1.

above, although good spontaneous generation of heat followed the quenching.

The three bars were again heated to complete decalescence and annealed in the furnace so as to leave all twelve bars of "specimen B" in annealed condition.

Fig. 1 is the curve sheet of "specimen B." "Galvanometer deflection" measures temperature difference, indicated thermoelectrically, between the steel under examination and a thermally equivalent quantity of water, contained separately in silvered Dewar vacuum jars. Both the steel and the water were usually brought to the same room temperature before being placed in the calorimeter. Fifty-five scale divisions indicate a temperature difference of 1° C.

The curve of normal cooling runs out of the figure at the upper left hand corner, and is easily distinguished from the others. This curve was obtained from a quantity of untreated steel equal in weight to "specimen B," and warmed a few degrees above room temperature before being placed in the calorimeter. It shows the normal loss of heat due to imperfect thermal insulation alone, and is the basis of comparison for all the other curves. Obviously this curve may be plotted further to the right or left without impairing its validity; and it may be plotted to intersect any of the other curves at any desired point, to facilitate study of the other curve at and near the intersection. For my own convenience I have constructed a metal template of the normal cooling curve, and find it most useful. Of course it is necessary that the base of the template be always kept coincident with the base line of the curve sheet.

The curve of "first hardening" shows the spontaneous generation of heat which followed the first quenching at about 777°, the temperature of complete loss of magnetic susceptibility, after which the scleroscope hardness must have been about 74.

The curve of second hardening, indicated by "*2h*," shows considerably greater generation of heat. Quenching temperature and hardness were not observed; but it is known that the quenching temperature was much higher than 777°.

The three curves thus far discussed were shown in the "second paper" already referred to, and the other curves here shown were subsequently plotted on the original curve sheet.

The third curve showing spontaneous generation of heat is indicated by "3*q*," meaning third quenching (not hardening). To make it clear that heat was generated in this case I have drawn the curve of normal cooling in a position for easy comparison (the upper dotted line). The "3*q*" curve was described in the second paper, but not plotted. The quenching temperature in this case must have been slightly below 660°, and hardness only about 37.

"Specimen B," left in the annealed condition at the close of former experiments, with a hardness of 31, was next gradually heated to 554°, allowed to cool slowly to 532° and quenched. It was then purposely brought to a temperature slightly above room temperature and placed in the calorimeter. The progress of cooling is plotted in the curve "$4q$" (fourth quenching). For easy comparison the normal cooling curve is drawn as a dotted line through the first station of the $4q$ curve. Beyond this point the $4q$ curve lies everywhere *below* the normal cooling curve, showing conclusively that the steel cooled abnormally fast. In other words, there was spontaneous disappearance or *absorption* of heat in the steel, most notable during the first few hours after quenching. Hardness was 35.5.

The result of this experiment is remarkable, and was quite unlooked for. I had expected to find a small generation of heat, if anything.

The steel was next heated to 562° and quenched. The result of this treatment is shown in the curve "$5q$," with its own dotted normal cooling curve. Absorption of heat is again indicated, even greater than in $4q$ but somewhat differently distributed. Hardness was now 34.5.

Again the steel was heated, this time to 594°, and quenched. Again there was marked absorption of heat. The curve, $6q$, was almost identical with $4q$, and is not plotted, to avoid confusion of lines. Hardness was again 34.5.

The seventh heating was carried to 667° for quenching. This was a much larger temperature advance than in either of the preceding experiments, and was *above the temperature of the third quenching,* which was followed by very considerable *generation* of heat. But now there was very considerable *absorption* of heat, as shown in curve "$7q$." Hardness was now 34.

It should be noted that the quenchings which were followed by absorption of heat were made at *rising* temperatures which had not been exceeded (except slightly in the case of $4q$) since the steel was annealed. But in the case of third quenching the quenching temperature was a falling one, reached by cooling from the much higher temperature of decalescence. I can think of no other cause than this for the radically different results of the third and seventh quenchings, which were made at substantially the same temperature. The temperature difference between complete loss and complete recovery of magnetic susceptibility, 117°, was unusually large; but while this temperature drop brought about almost annealed softness, and full restoration of magnetic qualities, it did not very greatly affect that quality of the steel, whatever it is, which is responsible for the spontaneous generation of heat. Seemingly, one or more of the several unstable compounds or mixtures of the constituents of the steel which were formed at the upper critical temperature did not have time to wholly revert to normal annealed condition while the metal was cooling to and passing through recalescence. The time of this cooling was about half an hour.

To confirm the curious result of the third quenching, *i. e.*, generation of heat without hardening, the bars were quenched the eighth time as follows: Slowly heated (nearly two hours) to 819°, slowly cooled (nearly one hour) to 680° and quenched. During the heating complete loss of magnetic susceptibility occurred at 779°, which was an excellent confirmation of the former finding (777°). But in cooling, full recovery of magnetic susceptibility came at 680°, which is 20° higher than before. The five intermediate treatments

RÉSUMÉ OF SPECIMEN B.

Temperature of complete loss of magnetic susceptibility, 777° C.
Temperature of complete recovery of magnetic susceptibility, 660/680.

	Quenching Temp.	Hardness.	Remarks.
First hardening....	About 777° C.	74	Good generation of heat
Second "	Much higher temp.	—	Much larger generation of heat
Third quenching ...	About 780°/660°	37	Fairly good " " "
Annealing.........		31	
Fourth quenching..	554°/532°	35.5	Good absorption of heat
Fifth " ..	562	34.5	" " " "
Sixth " ..	594	34.5	" " " "
Seventh " ..	667	34	" " " "
Eighth " ..	819°/680°	47	" generation " "

may, perhaps, account for this. And this higher quenching temperature may account for the somewhat greater hardness produced, which was later found to be 47, as against 37 for the third quenching (74 for true hardening above decalescent temperature).

Following the eighth quenching there was *good generation of heat,* better than after third quenching, but differently distributed in time—not so rapid at first, but much better sustained (curve not plotted). This appears to confirm the third experiment.

I cannot, thus far, offer any promising explanation of the absorption of heat in the fourth, fifth, sixth and seventh experiments.

It may be seen that absorption was rapid during the first few hours, and nearly (not quite) ceased at the end of 50 or 60 hours; while generation was well marked up to 150 hours. In earlier experiments generation of heat was easily detected at the end of a month.

As it seemed desirable to learn whether plain carbon steel would show, like the nickel-chromium steel, generation of heat without hardening, or absorption of heat when quenched at rising tempera-

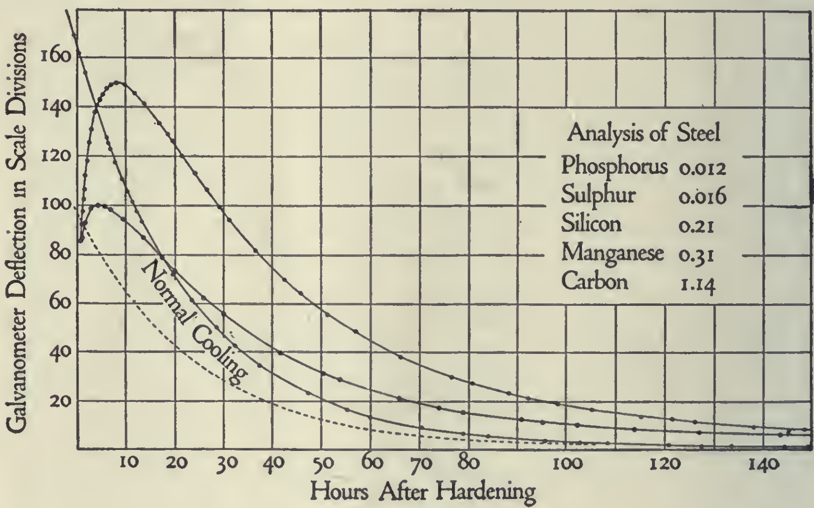

FIG. 2.

tures below the lower critical temperature, after annealing, the following experiments were made with the carbon steel used for the first experiment described in the first paper of the series. The normal cooling curve and upper curve of heat generation shown in Fig. 2 are taken from that paper.

Following is a résumé of the early and recent experiments with the carbon steel:

First (*Original*) *Hardening.*—Quenched at very high temperature. Temperature and hardness not then observed. Large generation of heat, as shown in upper curve of Fig. 2. Scleroscope hardness, recently observed, 79.

Second (*Recent*) *Hardening.*—Quenched at 802°, considerably above decalescence, but much lower than in first hardening. Complete loss of magnetic susceptibility occurred at *765°*. Good generation of heat, but very much less than in first, as shown by the lower curve of Fig. 2. For convenient comparison with this curve the normal cooling curve is shown as a dotted line appropriately located. Hardness was now 73.

Third Quenching.—Heated to 815°, somewhat above preceding quenching temperature, allowed to cool slowly to 720° and quenched. This was a *little below* the temperature of complete recovery of magnetic susceptibility, which had occurred at *729°*. Hardness was now only 28.5, and there was *no generation of heat.* (The nickel-chromium steel had shown good generation of heat under similar circumstances.) Note the small temperature difference, 36°, between complete loss and complete recovery of magnetic susceptibility. Annealed by heating to 822°, to obliterate previous quenching effects, and cooling slowly in furnace. Hardness was now 25.5.

Fourth Quenching.—Heated slowly, from annealed condition, to 633° (considerably below the lower critical temperature) and quenched. Hardness was again 28.5, and there was *no trace of absorption of heat.* (The nickel-chromium steel had shown good absorption of heat under similar circumstances.)

Fifth Quenching.—Heated slowly to 732°, just above the temperature of complete recovery of magnetic susceptibility, and quenched. No generation or absorption of heat, nor change in hardness (28.5).

Clearly, the carbon steel showed none of the excentricities of the nickel-chromium steel when quenched below the hardening temperature. But when quenched a little above, as well as far beyond this temperature, they behaved very much alike.

While considering plain carbon steel, I thought it worth while to observe heat generation in some steel (or white cast iron) very high in combined carbon, and very pure otherwise, which I happened to have in my laboratory. Fig. 3 shows the composition of this metal, which is hard and very brittle. The carbon is all combined, and remains so after heating and quenching.

An induction experiment with a large lump of the metal showed: Temperature of complete loss of magnetic susceptibility 757°.

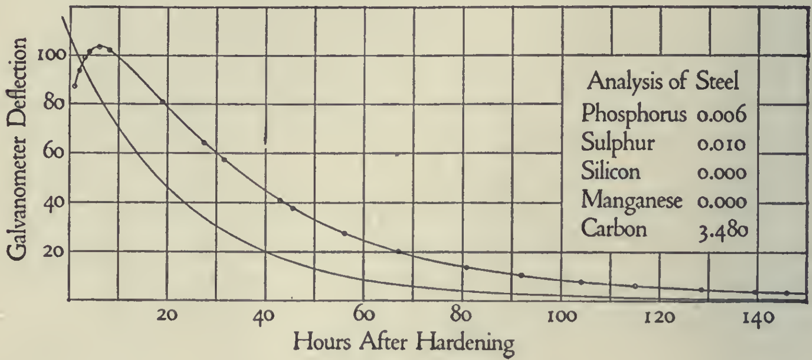

FIG. 3.

Temperature of complete recovery of magnetic susceptibility 704°:

Slowly heated many fragments, aggregating in weight that of the usual twelve bars of steel, to 906° and quenched.

Very moderate generation of heat followed the quenching, as shown in Fig. 3, and it was much less persistent than usual, as indicated by its small value at the end of 150 hours. Hardness was 76.

The behavior of this specimen of steel, or white cast iron, was not thought sufficiently encouraging to warrant further experiments with it.

For a general check on the performance of the apparatus, twelve half inch round bars of Swedish charcoal iron, of the aggregate weight of the steel usually employed, were slowly heated to 960° and quenched. Complete loss of magnetic susceptibility had occurred at 801°. The bars were warmed about three degrees just before being placed in the calorimeter.

There was no trace of heat generation following the quenching. Indeed, the curve of cooling followed the normal cooling curve with such fidelity that nowhere did they differ as much as the width of the curve line. This was very gratifying in view of the fact that observations for the normal cooling curve were made more than two years ago, and checked only once since that time.

Hardness was 18.5.

Again heated above decalescence and annealed by cooling in the furnace.

Hardness remained 18.5, showing that the previous heating and quenching had no effect whatever on the hardness of this, presumably, very pure iron.

Spontaneous generation and absorption of heat in recently quenched nickel-chromium steel, would be a better descriptive title for the present paper; but the subject matter is so intimately related to that of the former papers, that it is thought best to retain the former title for the sake of continuity.

In conclusion, I can only express the hope that contemplated experiments, on somewhat different lines, may throw more light on these interesting phenomena.

Cleveland, O.,
April, 1917.